

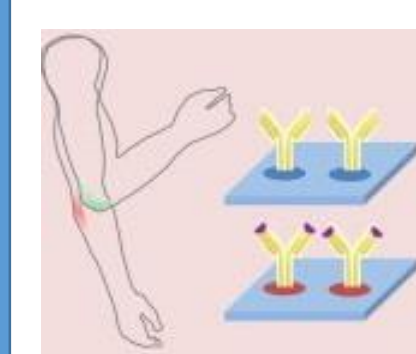


# Organic Small Molecule Mechanofluorochromic Dyes: Synthesis, Optical Responses in Varying Macromolecular Environs and Prospective Application in Flexible Sensors

Rakesh R<sup>1</sup>, Manjinder Singh<sup>1</sup>, Mrudul C<sup>1</sup>, Lakshmi S<sup>2</sup>, Parvathy VS<sup>3</sup> and KG Sreejalekshmi<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Indian Institute of Space Science and Technology, Valiamala PO, Thiruvananthapuram, India 695 547; <sup>2</sup>Department of Chemistry, Pondicherry University, Puducherry, India 605014; <sup>3</sup>Department of Chemistry, Amrita University, Amritapuri, Kollam, India 690525 \*email: [sreeja@iist.ac.in](mailto:sreeja@iist.ac.in)

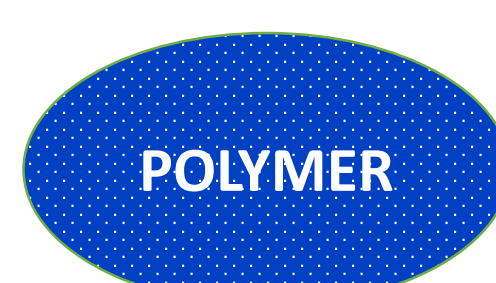
## INTRODUCTION



Mechanochromic system in healthcare



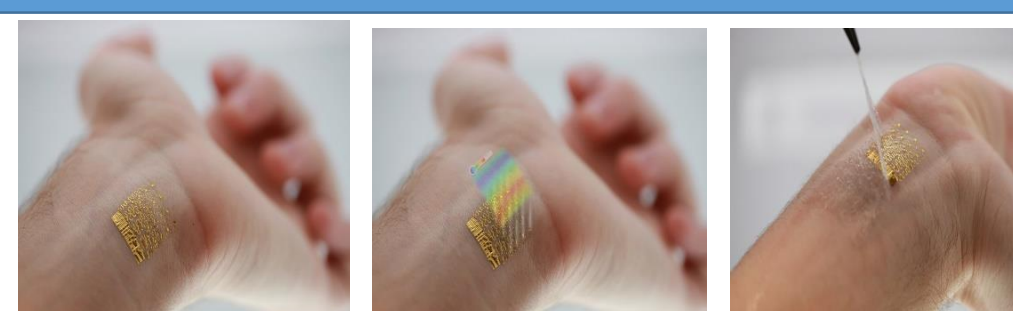
Mechanochromic helmet to alert athletes to potential brain trauma



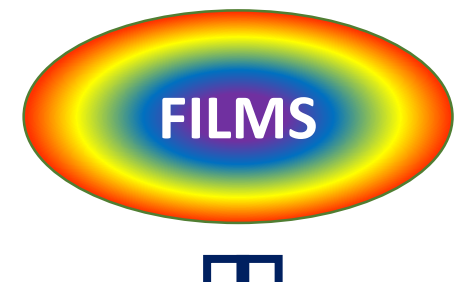
POLYMER



DYE



Ultrathin, compliant, skin-like arrays of precision temperature sensors and heaters



FILMS

### Polymer-based Mechanochromic materials

- Conformational change of polymers
- Aggregation based responses
- Mechanically induced cleavage of covalent or noncovalent bonds

### Polymer-based Thermochromic materials

- Influencing the proton equilibrium of indicator dyes embedded in polymer networks

### MECHANOCHROMISM

- ❖ Prediction of mechanical failure
- ❖ Mechano- and pressure sensors
- ❖ Indicators of mechano-history
- ❖ Security plastics and papers
- ❖ Data storage devices

### THERMOCHROMISM

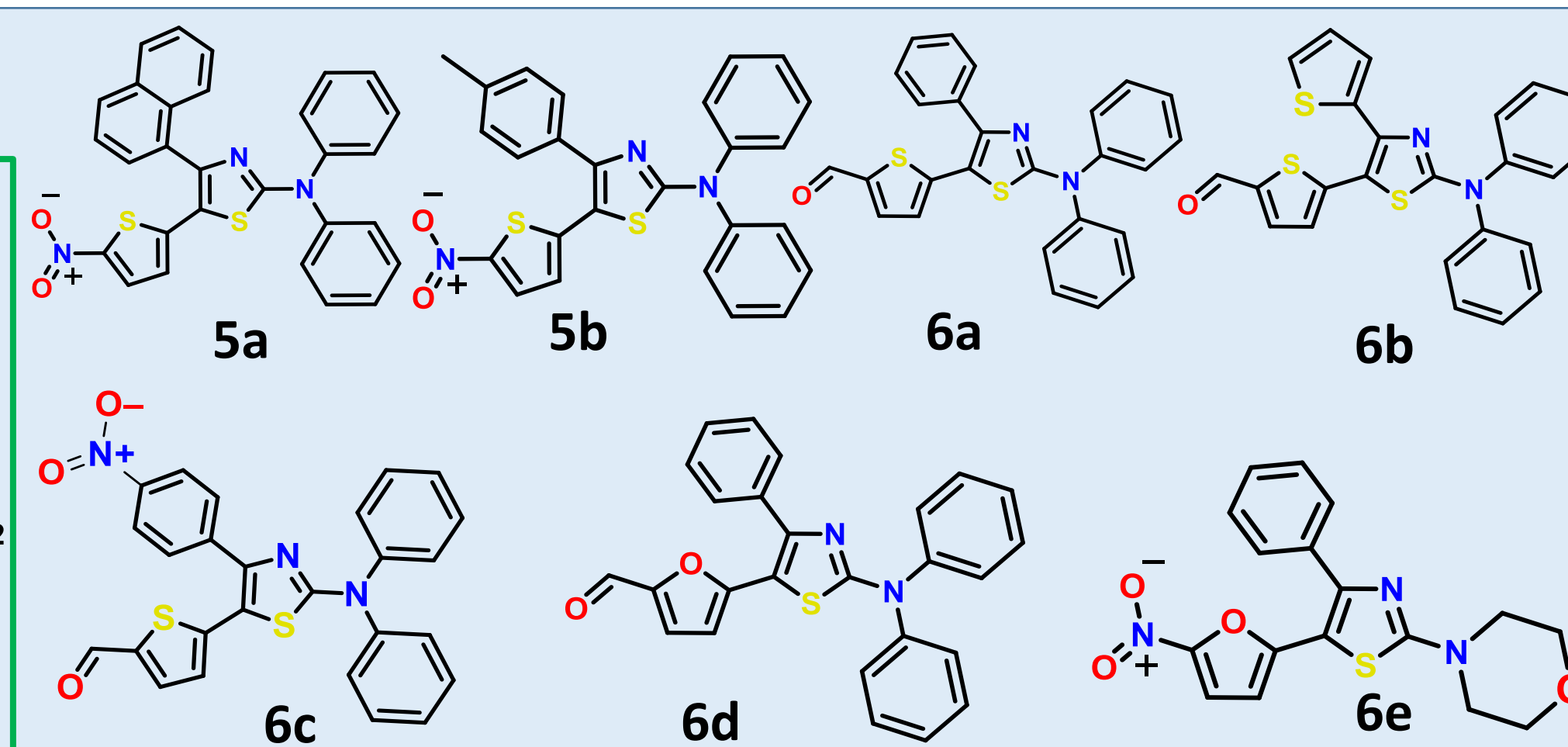
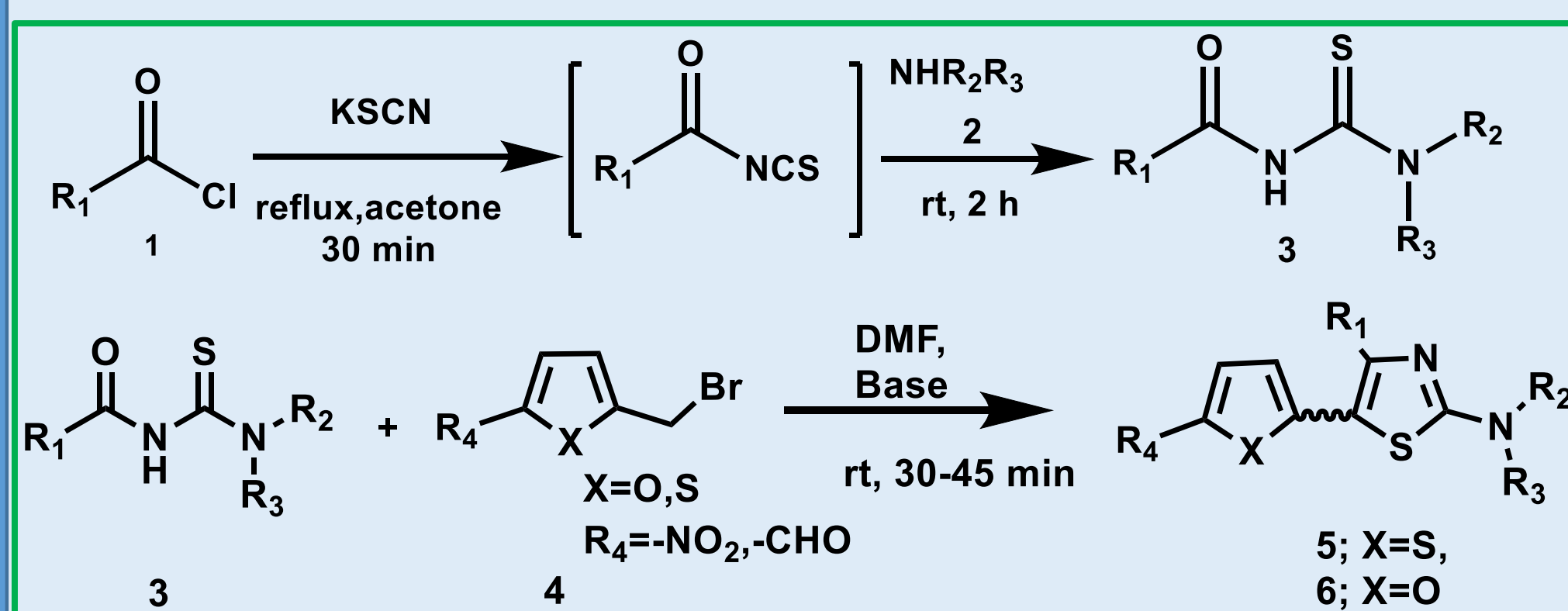
- ❖ Smart labels indicating thermal history
- ❖ Temperature sensors without an external electrical power source
- ❖ Time-temperature indicators

## OBJECTIVES

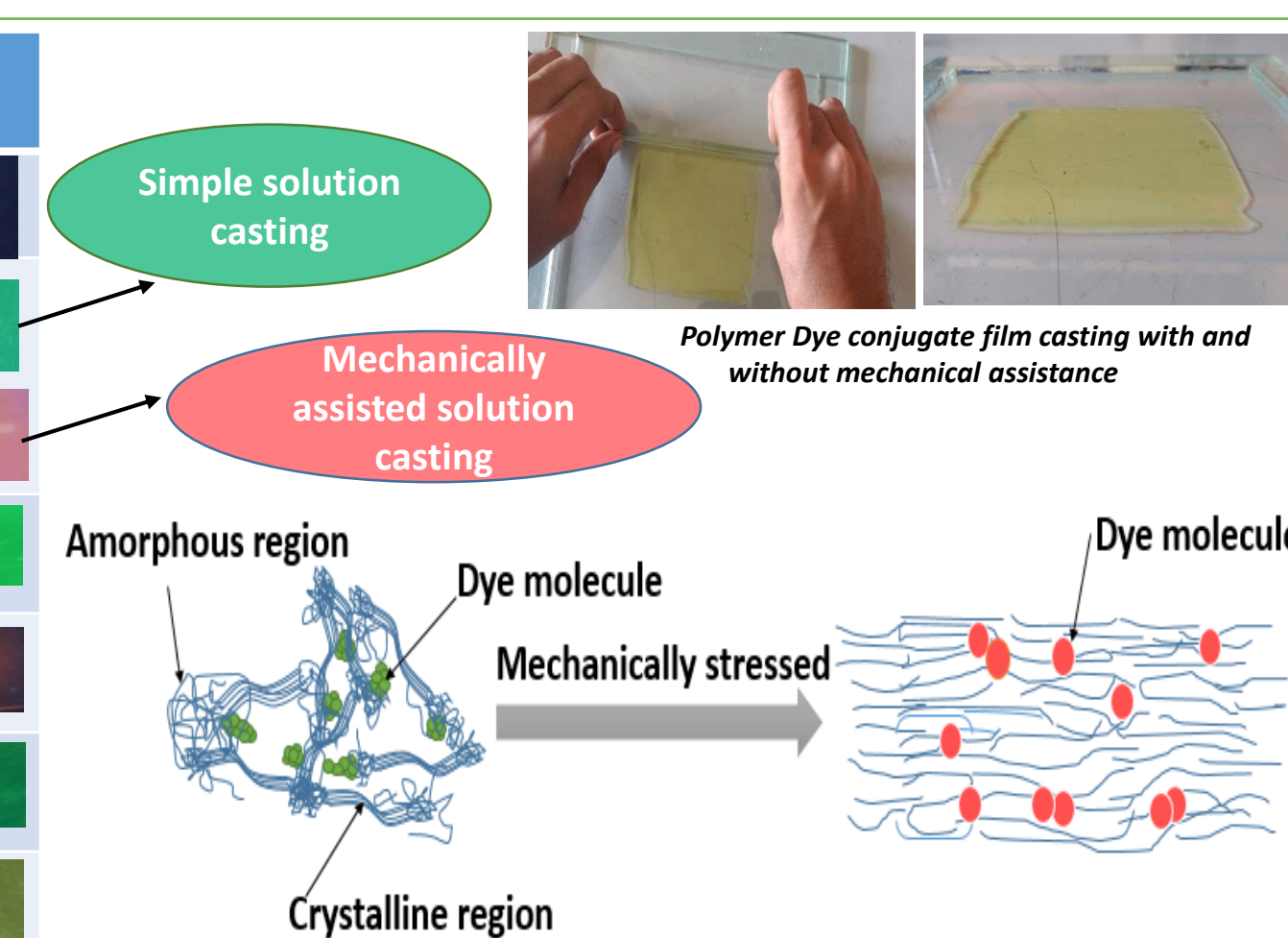
- Design and synthesis of novel mechanochromic multiheterocyclic dyes
- Study of photophysical properties of the dyes
- Preparation of polymer dye conjugate by physical dispersion in various polymer matrix and characterization
- Studying the effect of varying macromolecular environments on the photophysical properties of the dyes
- Study the stimuli-responsiveness (mechanical stress, heat, light) on the prepared polymer films
- Exploring the potential of the films for application in prospective flexible sensors

## SYNTHESIS

### Synthesis of dye



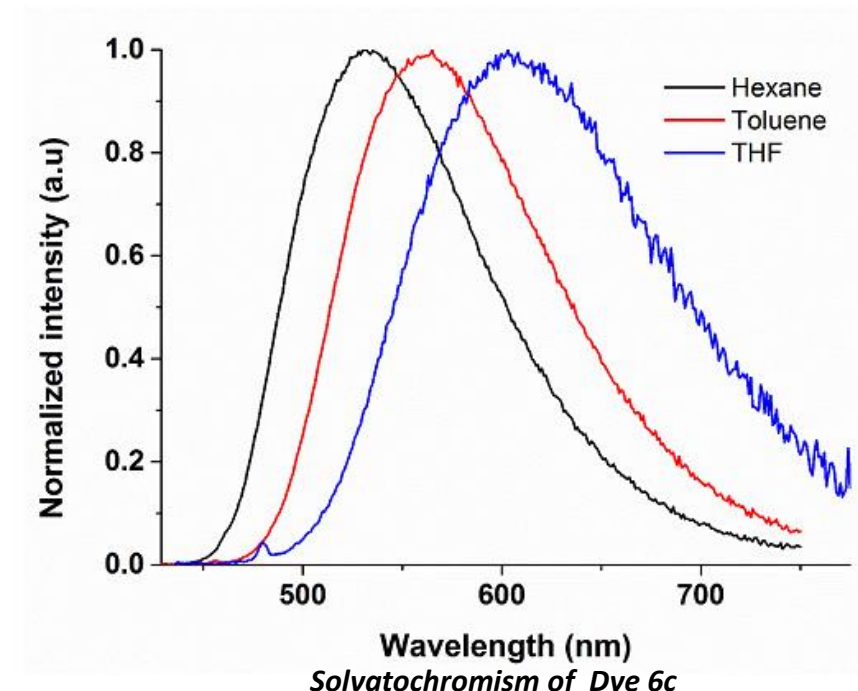
POLYMER	DYE	FILM
PVDF	DYE 5a	
PVDF	DYE 6a	
PU	DYE 6a	
PMMA	DYE 5a	
PMMA	DYE 6a	
PDMS	DYE 5b	



## Photophysical properties of Dye molecules

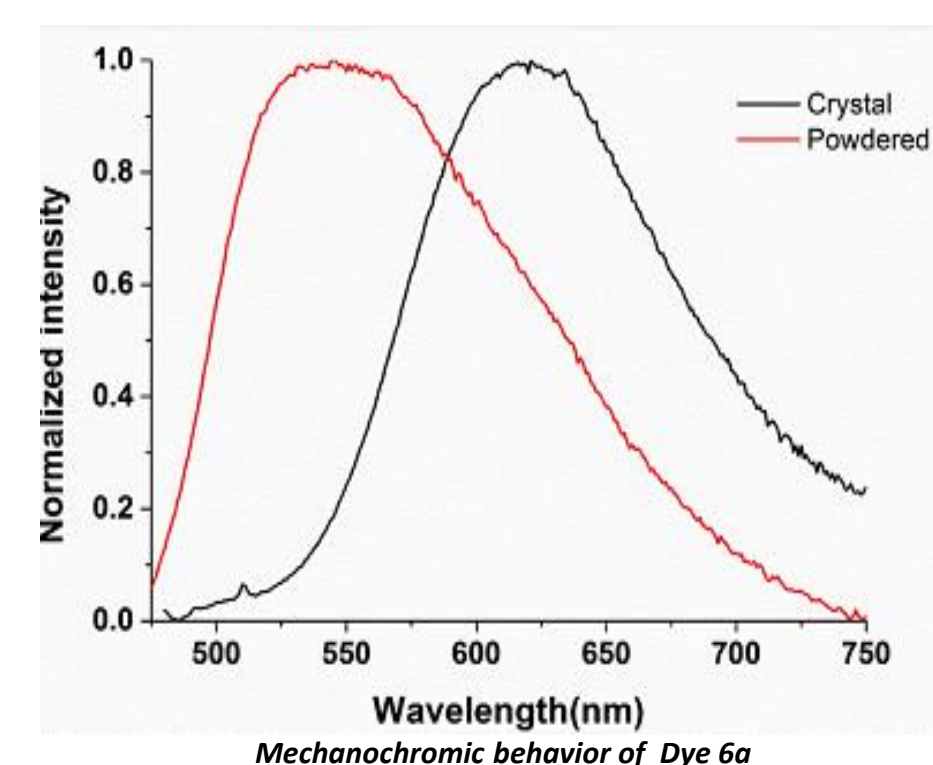
No	Code	Toluene				THF			
		$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	SS (nm)	QY	$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	SS (nm)	QY
1	5a	457	574	117	0.40	455	601	146	0.37
2	5b	461	578	117	0.64	466	602	136	0.15
2	6a	412	511	99	0.09	409	521	112	0.03
3	6b	416	522	106	0.05	409	523	114	0.06
4	6c	415	565	149	0.28	410	603	193	0.02
5	6d	397	484	87	0.01	395	484	89	0.01
6	6e	391	463	72	0.01	389	468	79	0.01

### Solvatochromism

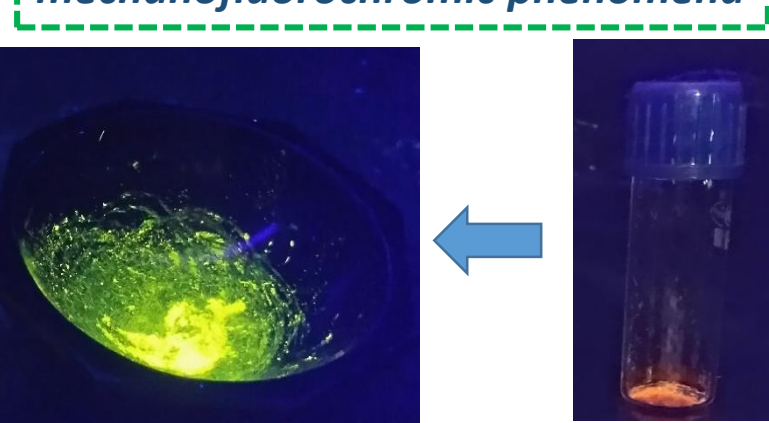


Solvatochromism of Dye 6c in hexane, toluene and THF under UV light

### Mechanofluorochromism



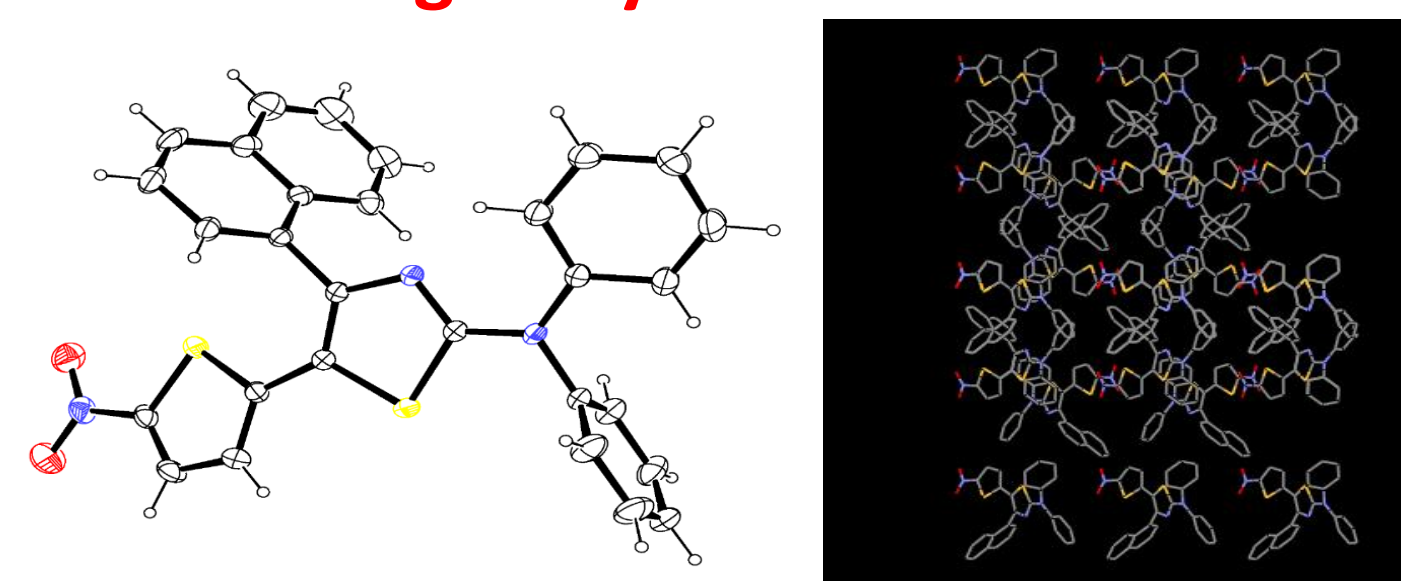
All the aldehyde substituted molecules are characterized by mechanofluorochromic phenomena



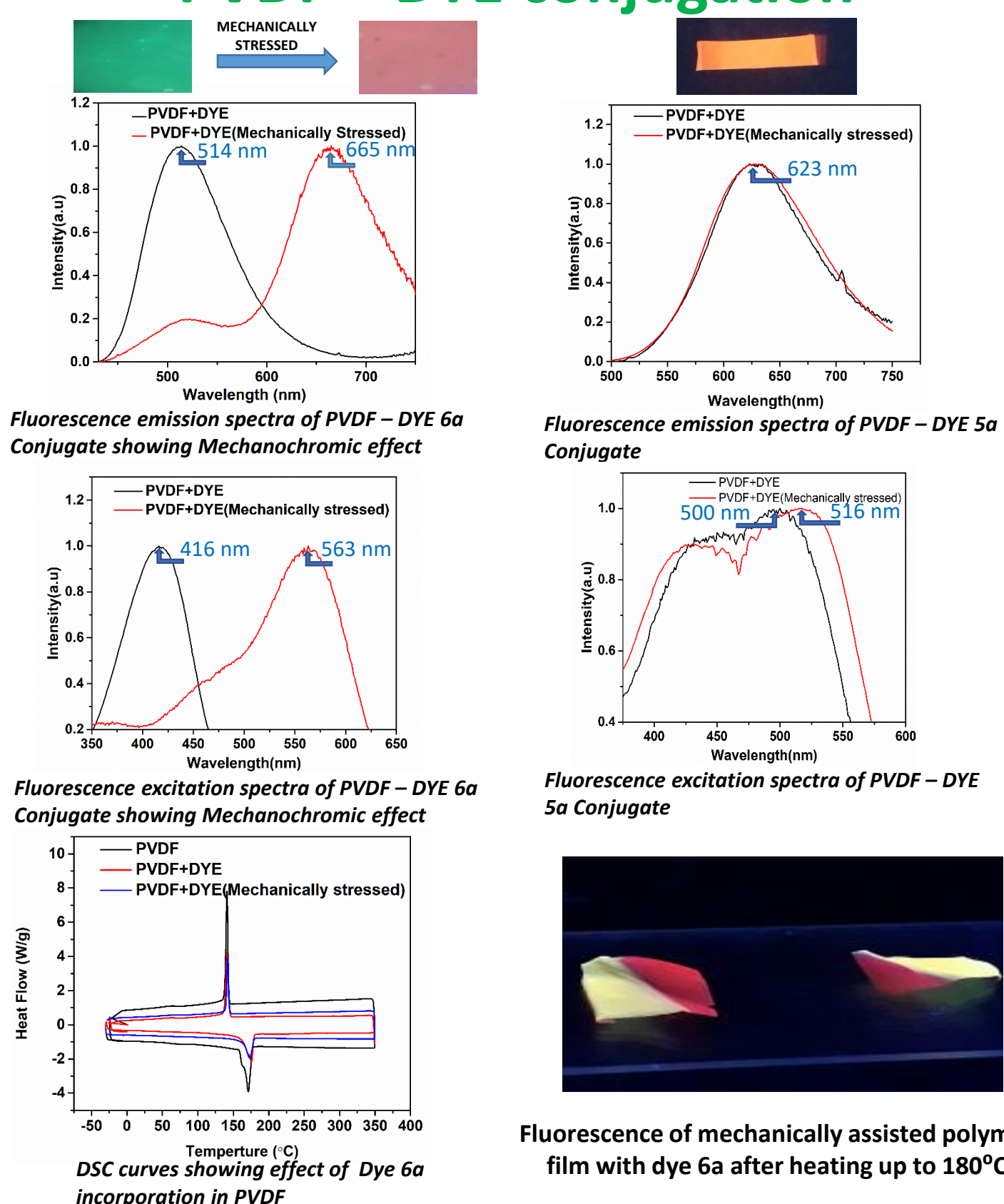
Powder (left) and crystal (right) samples of dye 6a under UV light

## RESULTS AND DISCUSSION

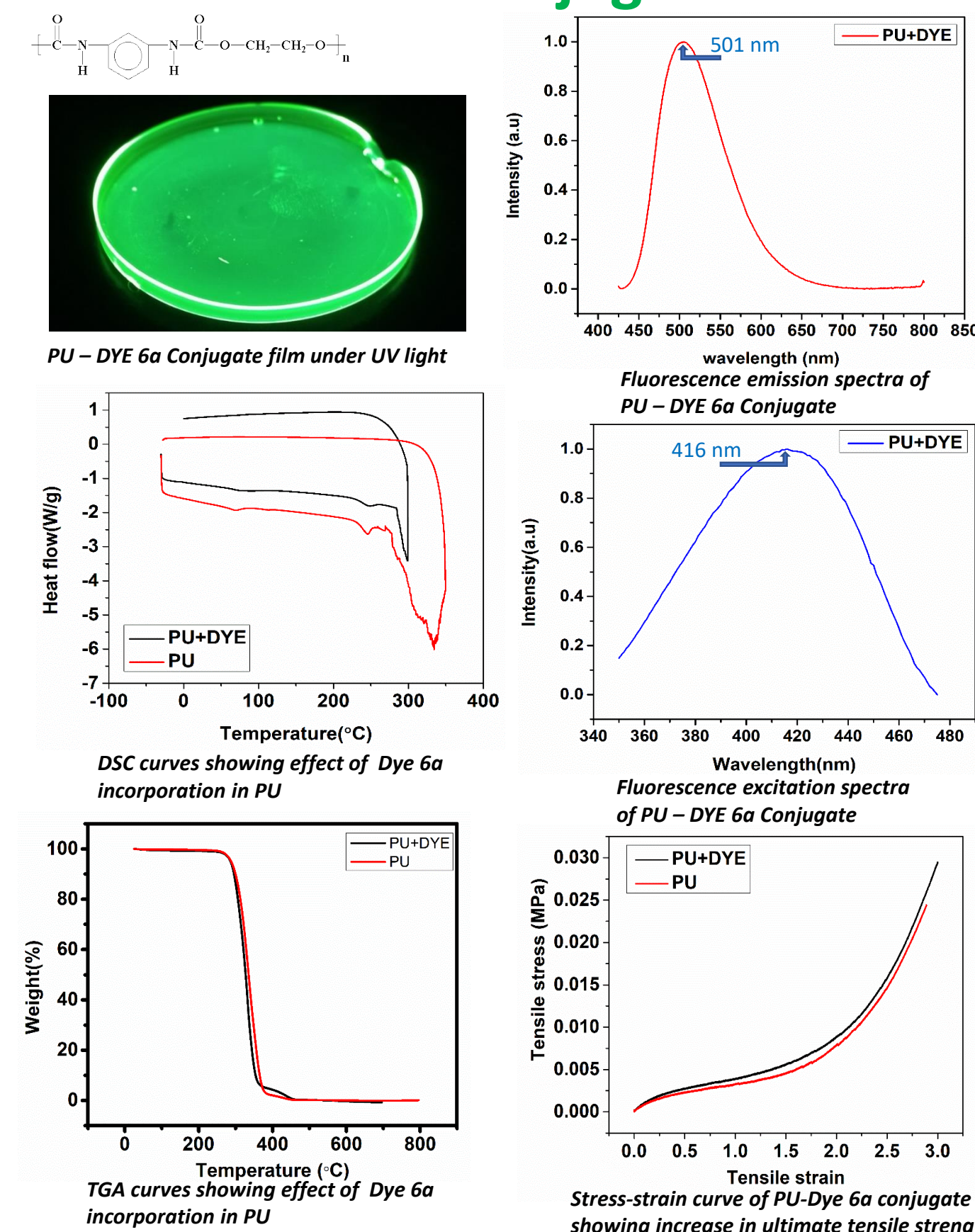
### Single Crystal XRD



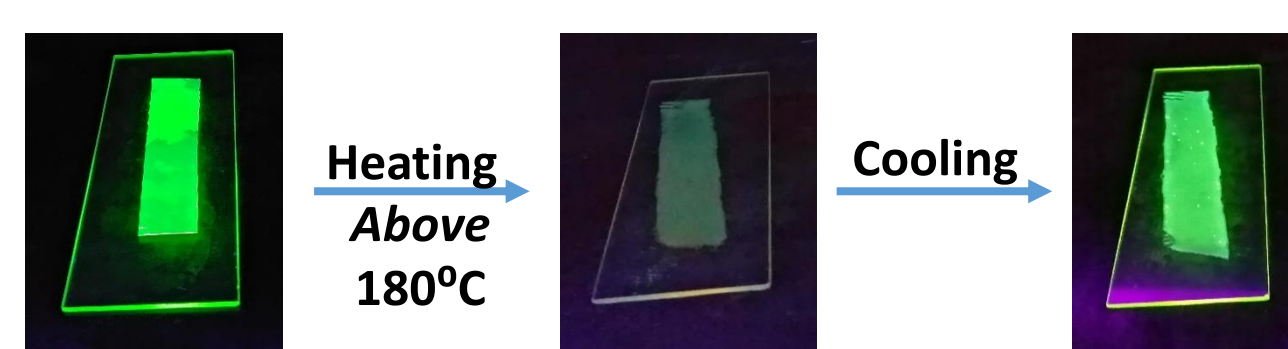
### PVDF – DYE conjugation



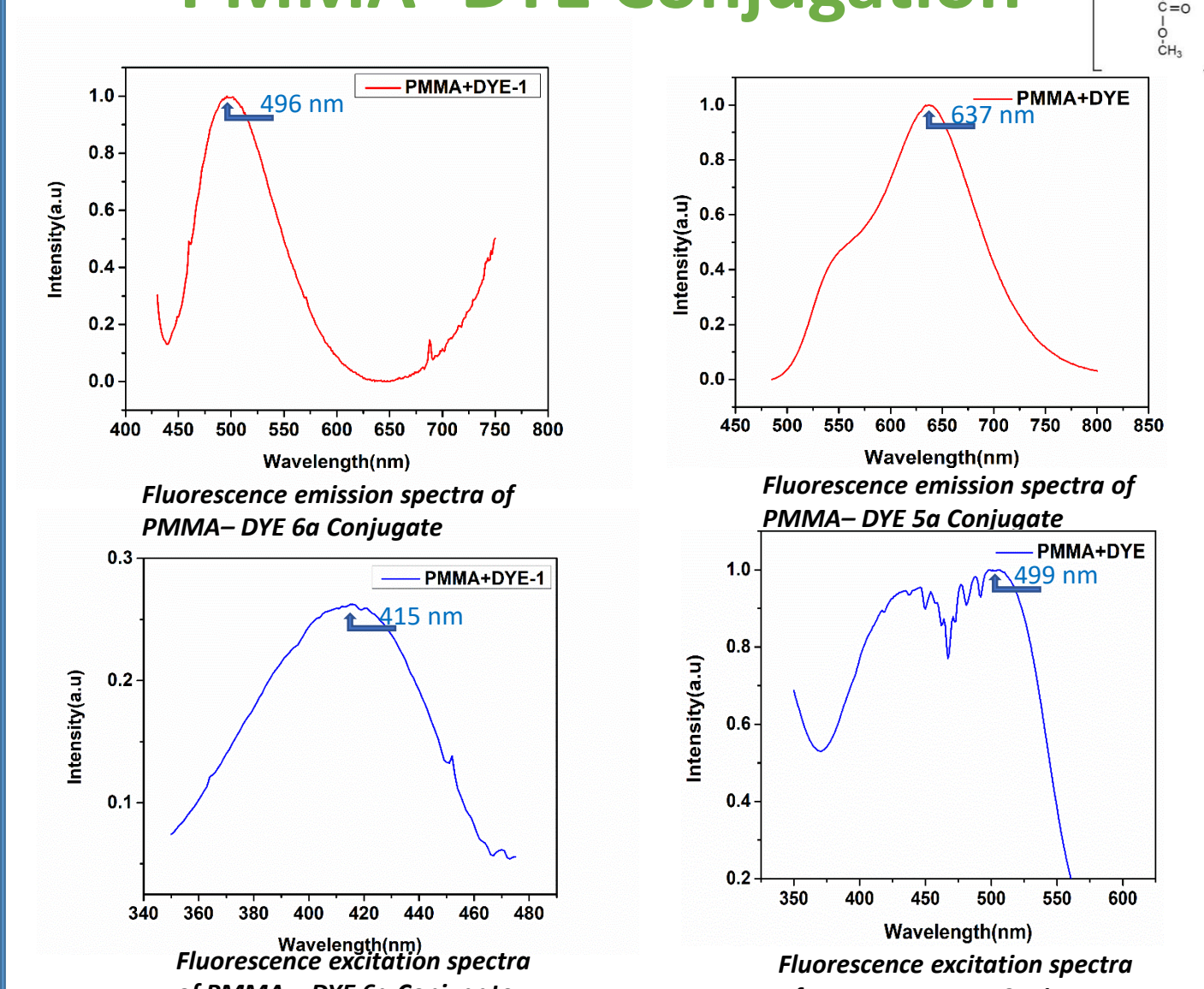
### PU – DYE conjugation



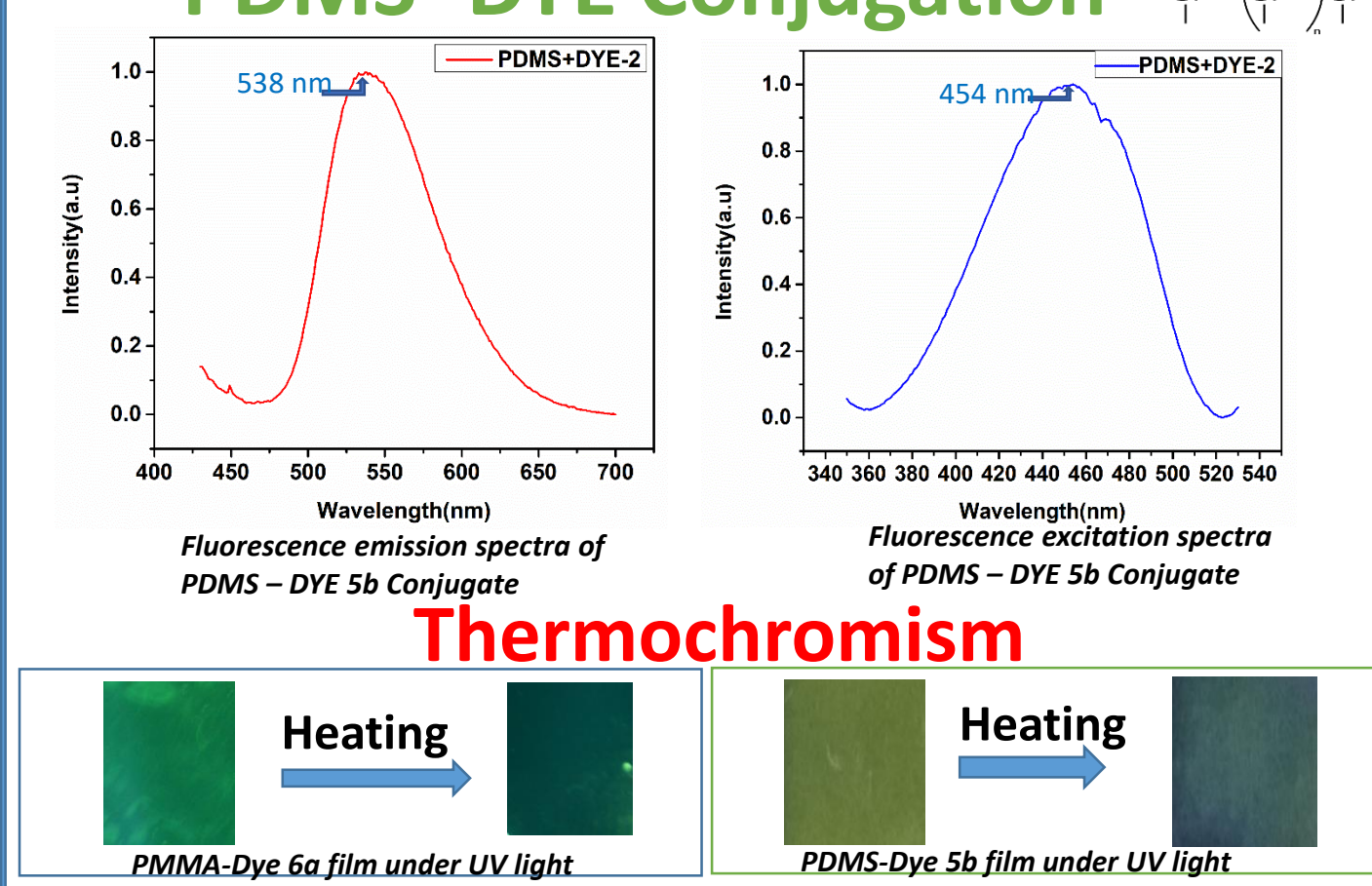
### Reversible Thermochromism



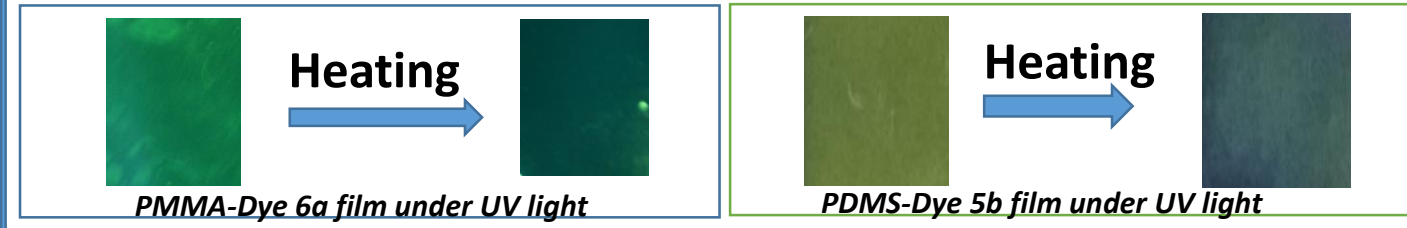
### PMMA- DYE Conjugation



### PDMS- DYE Conjugation



### Thermochromism



## CONCLUSIONS

- We designed and successfully synthesized a novel family of 5-heteroaryl-1,3-thiazole dyes with mechanochromic properties
- Polymer-dye conjugates using various combinations of dye-macromolecular environs (PVDF, PU, PDMS and PMMA) were prepared
- PVDF-Dye conjugate exhibited variation in optical responses with preparation methods
- Photophysical properties, thermal behavior and mechanical properties of polymer-dye conjugates were studied
- Surprisingly, dye 6a inhibited the curing of PDMS even after prolonged periods of curing
- PU-dye 6a conjugate films showed reversible thermochromism over repeated cycles
- Development of these polymer-dye conjugate for application in flexible sensors are actively pursued in our laboratory

## REFERENCES

- Radhakrishnan, R.; Sreejalekshmi, K. G. *RSC Adv.*, 2016, 6, 32705–32709
- C. Weder, S. Schretil, *Journal Of Polymer Science, Part A: Polymer Chemistry* 2017, 55, 640–652
- A. Seeboth, D. Lotzsch and R. Ruhmann, *J. Mater. Chem. C*, 2013, 1, 2811
- D. Galliani, L. Mascheroni, M. Sassi, R. Turrisi, R. Lorenzi, L. Beverina *Adv. Optical Mater.* 2015, 3, 1164–1168
- Webb, R. C., Bonifas, A. P., Behnaz, A., Zhang, Y., Yu, K. J., Cheng, H., et al. *Nature Materials*, 2013, 12(10), 938.

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